In Table I the values of ΔE in other systems obtained by other researchers are also listed and these data reveal that the foregoing assumption on the strength of hydrogen bonding power of antipyrine may be fairly accurate, but these values are far different between researchers. It may be summarized that the hydrogen bonding power of antipyrine or aminopyrine with proton donors is considerably strong and nearly equal to that of ethyl ether, dioxane, or pyridine. It may be expected that molecular addition compounds would be formed, with strong intermolecular hydrogen bond, with compounds containing active hydrogen.

The authors wish to express their sincere gratitude to Prof. S. Takagi of the University of Kyoto for his helpful guidance, and to Messrs. K. Ōya, Y. Yamaguchi, H. Yamura, S. Yoshida, and H. Yoshida of this Company for their kind encouragements.

Experimental

The spectra were obtained with a Perkin-Elmer Model 21 recording infrared spectrophotometer, using NaCl prism.

All of the substances studied were commercially available. These compounds were used without further purification unless doubt exsisted as to their purity, and if purification was necessary, standard methods of distillation and recrystallization were used.

Summary

The hydrogen bonding power of antipyrine and aminopyrine was examined by the measurement of infrared absorption spectra of various ternary solutions and it was concluded that the molecular complexes $C_6H_5OH\cdots OC(C_{10}H_{12}N_2)$ and $C_6H_5OH\cdots OC(C_{12}H_{17}N_3)$ formed in the solution by intermolecular hydrogen bonding. The order of the strengths of these hydrogen bond was considerably large.

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22. **Naofumi Ōi, Kazuko Kageyama, and Keiichiro Miyazaki :** Studies on Intermolecular Bonds by Infrared Absorption Spectra. II.[1] Hydrogen Bonding Power of Santonin.

(*Research Department, Osaka Works, Sumitomo Chemical Co.**)

Kakemi, *et al.*[2] studied molecular addition compounds of santonin with various resorcinol derivatives by thermoanalyses, but the structure of the molecular compounds was not examined. In this paper the hydrogen bonding power of santonin is presented for studying its intermolecular bonds.

In the previous paper,[1] we reported the hydrogen bonding power of antipyrine and aminopyrine by the infrared absorption spectra, and the same method was used in this study.

The infrared absorption spectra were measured in the region of 3000~4000 cm^{-1} and 1500~2000 cm^{-1} in three ternary solutions.

The compositions of the ternary solutions examined were phenol, thymol, and 1-naphthol, each with santonin and carbon tetrachloride.

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1) Part I : This Bulletin, **5**, 141(1957).

2) K. Kakemi, T. Uno, Y. Sanada : Archive of Practical Pharmacy, **12**, 52(1953).

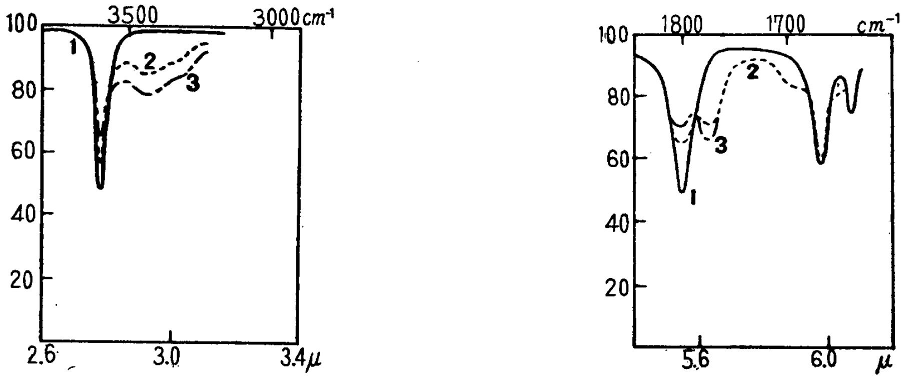
For comparison, infrared absorption measurements were made also of binary solutions of phenol, thymol, 1-naphthol, and santonin each with carbon tetrachloride.

These spectra of three ternary solutions were very similar. In Fig. 1, as an example, the spectra of ternary solutions of thymol, santonin, and carbon tetrachloride are shown.

These figures show how the absorption of santonin is affected by the addition of a proton-donor and the absorption of thymol affected by the addition of santonin to the solution.

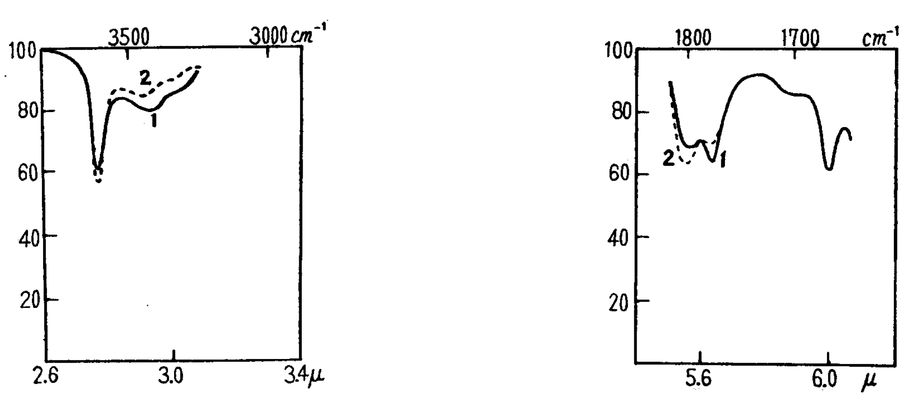
In Fig. 1 thymol has only one OH band at 3593 cm^{-1} and santonin has two CO bands at 1799 and 1667 cm^{-1} in the binary solutions, but in the ternary solutions two OH bands are present, one at 3593 and the other at 3289 cm^{-1}, and three CO bands are present at 1799, 1774, and 1667 cm^{-1}.

The comparison of these curves reveals that by adding santonin to the solution of thymol, the absorption intensity of the OH band at 3593 cm^{-1} becomes weaker and there appears another OH band at 3289 cm^{-1}. Further experiments have shown that, on increasing the concentration of santonin in the solution, there occurs a decrease in the absorption intensity of 3593 cm^{-1} and an increase in that of 3289 cm^{-1}. Moreover,



Thymol concn., 0.01 mol./L.
No. Santonin concn.
1 Nil
2 0.002 mol./L.
3 0.006 mol./L.
Temp. ~20° Cell, 10 mm.

Santonin concn., 0.008 mol./L.
No. Thymol concn.
1 Nil
2 0.067 mol./L.
3 0.133 mol./L.
Temp. ~20° Cell, 0.5 mm.



Thymol concn., 0.01 mol./L.
Santonin concn., 0.006 mol./L.
No. Temp.
1 ~20°C
2 ~50°C
Cell, 10 mm.

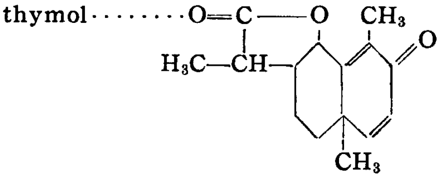
Santonin concn., 0.008 mol./L.
Thymol concn., 0.133 mol./L.
No. Temp.
1 ~20°C
2 ~50°C
Cell, 0.5 mm.

Fig. 1. Santonin + Thymol + CCl_4

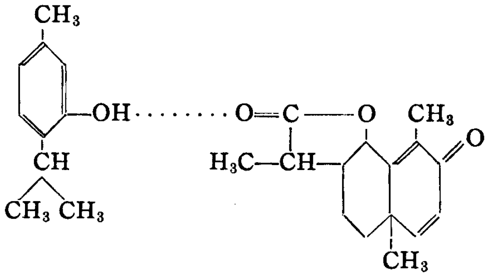
on raising the temperature of the ternary solution there occurs an increase in the absorption intensity of the band at 3593 cm^{-1} and a decrease in that of 3289 cm^{-1}, but no shift occurs in the positions of these OH bands.

These facts may be interpreted as indicating the formation of intermolecular hydrogen bond R–OH····santonin in the above-mentioned ternary solutions.

On the other hand, on adding thymol to the solution of santonin, the absorption intensity of the CO band at 1799 cm^{-1} becomes weaker and there appears another CO band at 1774 cm^{-1} and scarcely any change occurs in the CO band at 1667 cm^{-1}. Further experiments have shown that, on increasing the concentration of thymol in the solution, there occurs a decrease in the absorption intensity of the band at 1799 cm^{-1} and an increase in that of the 1774 cm^{-1} band. On raising the temperature of the ternary solution, there occurs an increase in the absorption intensity of 1799 cm^{-1} band and a decrease in the 1774 cm^{-1} band, but no shift occurs in the positions of the CO bands. Santonin has two CO groups, one of which is a lactone type and the other is a ketone type, and the CO band at 1799 cm^{-1} is that of the lactone and that at 1667 cm^{-1} is of the ketone. These facts may be interpreted as indicating the formation of the following intermolecular hydrogen bond in the above-mentioned ternary solutions.



Therefore, it was concluded that in this ternary solution the following molecular



complex would be formed by the intermolecular hydrogen bonding and that their complex molecule consists of free thymol and santonin molecules in equilibrium :

$$C_{10}H_{13}OH + OC(C_{14}H_{18}O_2) \rightleftarrows C_{10}H_{13}OH\cdots OC(C_{14}H_{18}O_2)$$

The spectra of ternary solutions in which phenol or 1-naphthol is present instead of thymol as a proton-donor, and santonin is present as a proton-acceptor, are much like those in Fig. 1 and similar interpretations may be given of these data.

In these three kinds of ternary solution, the values of ν_{OH} (the wave number of hydrogen-bonded OH stretching vibration), $\Delta\nu_{OH}$ (its shift from the wave number 3610 or 3593 cm^{-1} for free OH stretching vibration), ν_{CO} (the wave number of hydrogen-bonded CO stretching vibration), and $\Delta\nu_{CO}$ (its shift from the wave number 1799 cm^{-1} for free CO stretching vibration) are given in Table I.

TABLE I.

Proton donor	Proton acceptor	ν_{OH}(cm^{-1})	$\Delta\nu_{OH}$(cm^{-1})	ν_{CO}(cm^{-1})	$\Delta\nu_{CO}$(cm^{-1})
Phenol	Santonin	3294	316	1774	25
Thymol	〃	3289	304	1774	25
1-Naphthol	〃	3284	326	1775	24

As mentioned in the previous paper,$^{1)}$ the order of the strengths of these hydrogen bonds in these complexes may be determined by observing the wave number of the OH bands related to the hydrogen bonds in question.

Examination of Table I and comparison with the data described in the preceding paper[1] reveal that the OH····O bonds in the complexes, thymol····santonin, etc., are stronger than the OH····O bonds in the complex, thymol····dioxane, ethyl ether, etc., and weaker than OH····O bonds in the complex, thymol····antipyrine, aminopyrine.

As an example of the determination of intermolecular hydrogen bond energy by calculation, ΔE between thymol and santonin was obtained after Tsuboi's method[3] according to the data of temperature change. The value obtained was $\Delta E \fallingdotseq -3$ Kcal./mole and this result indicates that the foregoing assumptions on the strength of hydrogen bonding power of santonin may be fairly accurate.

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[3] M. Tsuboi : J. Chem. Soc. Japan, **72**, 146(1951).